



# Photocatalytic reduction of nitrate ions to dinitrogen over layered perovskite $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ using water as an electron donor



Marie Oka<sup>a</sup>, Yugo Miseki<sup>a</sup>, Kenji Saito<sup>a,1</sup>, Akihiko Kudo<sup>a,b,\*</sup>

<sup>a</sup> Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

<sup>b</sup> Photocatalyst International Research Center, Research Institute of Science and Technology, Tokyo University of Science, 2641 Noda-shi, Yamazaki, Chiba-ken 278-8510, Japan

## ARTICLE INFO

### Article history:

Received 18 February 2015

Received in revised form 13 May 2015

Accepted 17 May 2015

Available online 19 May 2015

### Keywords:

Photocatalysis

Nitrate reduction

Dinitrogen

Boric acid

Layered perovskite material

## ABSTRACT

Photocatalytic reduction of  $\text{NO}_3^-$  to produce  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , and  $\text{N}_2$  proceeded on  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  powder under UV irradiation accompanied with photochemical decomposition of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  and  $\text{O}_2$  without any sacrificial reagents. Loading of Cu and Ni cocatalysts enhanced the photocatalytic reaction to form  $\text{N}_2$ . Ni was the most effective cocatalyst. The  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst with the Ni cocatalyst loaded by an impregnation method and subsequent  $\text{H}_2$  reduction showed high activity for the reduction of  $\text{NO}_3^-$  to form  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , and  $\text{N}_2$ .  $\text{O}_2$  also formed as an oxidation product of water. The ratio of the number of reacted electron to that of hole was almost unity, indicating water was consumed as an electron donor for the reduction of  $\text{NO}_3^-$ . A boric acid of a buffer for pH control was effective to obtain a high yield of  $\text{N}_2$ . The  $\text{N}_2$  yield reached 85% in the presence of a boric acid after 10 h using a 400 W high-pressure mercury lamp in 10 mmol/L of an aqueous  $\text{NaNO}_3$  solution, while it was 50% without the boric acid. The  $\text{N}_2$  yield was almost 100% when 3 mmol/L of an aqueous  $\text{NaNO}_3$  solution was used with a boric acid.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Nitrate ions contained in agricultural and industrial wasted water cause water pollution. Therefore, the development of efficient and clean processes for the elimination of nitrate ions has attracted attention. Electrochemical [1], photocatalytic [2–25], and biological [26] methods have been reported as the candidates for the process as well as a physical separation using a semipermeable membrane [27]. Among them, the photocatalytic process is very simple because just the dispersion of photocatalyst powder can be used: that is the significant advantage for the photocatalytic process.  $\text{TiO}_2$  [2–18],  $\text{ZnO}$  [19],  $\text{H}_4\text{Nb}_6\text{O}_{17}$  [6],  $\text{SrTiO}_3$  [2,4],  $\text{K}_x\text{Ga}_x\text{Sn}_{8-x}\text{O}_{16}$  [20], tantalates [21],  $\text{CdS}$  [22–24], and Ni-doped  $\text{ZnS}$  [25] have been reported as photocatalysts for reduction of nitrate ions.  $\text{ZnO}$  [19] with a wide band gap and  $\text{CdS}$  [2,22,23] with a visible light response are active photocatalysts for the reduction of nitrate ions to nitrite ions in the presence of reducing reagents

such as methanol without any cocatalysts.  $\text{TiO}_2$ ,  $\text{SrTiO}_3$ , and  $\text{CdS}$  photocatalysts can produce  $\text{NH}_3$  from  $\text{NO}_2^-$  [2]. Cocatalyst and reaction condition are important for the activity and selectivity of photocatalytic reduction of nitrate ions as for water splitting. For example, when  $\text{Cu}/\text{TiO}_2$  is used,  $\text{NH}_3$  and  $\text{NO}_2^-$  are obtained in acidic and basic aqueous solutions, respectively [8].  $\text{TiO}_2$  photocatalyst loaded with Cu-Pd alloy cocatalyst gives  $\text{NH}_3$  efficiently [13]. Photocatalysts that can reduce  $\text{NO}_3^-$  to  $\text{N}_2$  of a harmless product in the presence of sacrificial reagents are  $\text{TiO}_2$  co-loaded with Pd and Cu [8],  $\text{TiO}_2:\text{W},\text{N}$  [14],  $\text{H}_4\text{Nb}_6\text{O}_{17}$  [6], and  $\text{K}_x\text{Ga}_x\text{Sn}_{8-x}\text{O}_{16}$  [20] with UV light responses, and  $\text{ZnS}:\text{Ni}$  [25] with visible light response. However, a clean process should not require any sacrificial reagents. Noble metal cocatalyst-loaded  $\text{TiO}_2$  [3–5] and Ni cocatalyst-loaded tantalate [21] photocatalysts reduce  $\text{NO}_3^-$  in the absence of sacrificial reagents accompanied with  $\text{O}_2$  evolution of an oxidation product of water. Among them, Ni-loaded  $\text{KTaO}_3$  photocatalyst shows high activity that 44% of  $\text{NO}_3^-$  can be converted to  $\text{N}_2$  after 25 h using a 400 W high pressure mercury lamp [21]. We found that NiO-loaded  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst with layered perovskite structure shows high activity for water splitting into  $\text{H}_2$  and  $\text{O}_2$  in a stoichiometric amount [28]. The  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst powder with a plate-like shape reflecting the layered perovskite structure can be prepared by a polymerizable complex method. When Ag cocatalyst is loaded on the  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  powder, the photocatalyst is active for  $\text{CO}_2$  reduction into  $\text{CO}$  using water

\* Corresponding author at: Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan.  
Tel.: +81 3 5228 8267.

E-mail address: [a-kudo@rs.kagu.tus.ac.jp](mailto:a-kudo@rs.kagu.tus.ac.jp) (A. Kudo).

<sup>1</sup> Current address: Office for Development of Young Researchers, Research Planning and Promotion Division, Niigata University, 8050 Ikarashi 2-no-cho, Nishi-ku, Niigata 950-2181, Japan.

**Table 1**

$\text{NO}_3^-$  reduction over  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst with various cocatalysts.

| Cocatalyst<br>(wt%) <sup>a</sup> | Amounts of products after 10 h/ $\mu\text{mol}$ |              |                 |                 | Selectivity <sup>b</sup><br>% | $\text{N}_2$ yield <sup>c</sup><br>% | $e^-/\text{h}^+$ |  |  |
|----------------------------------|-------------------------------------------------|--------------|-----------------|-----------------|-------------------------------|--------------------------------------|------------------|--|--|
|                                  | Reduction product                               |              |                 |                 |                               |                                      |                  |  |  |
|                                  | $\text{H}_2$                                    | $\text{N}_2$ | $\text{NO}_2^-$ | $\text{NH}_4^+$ | $\text{O}_2$                  |                                      |                  |  |  |
| None                             | 0.3                                             | 13           | 1900            | 0               | 1300                          | 99                                   | 0.7              |  |  |
| Ni(0.5)                          | 5200                                            | 800          | 210             | 700             | 8300                          | 57                                   | 0.7              |  |  |
| Ni(1.0)                          | 3100                                            | 790          | 320             | 610             | 7000                          | 68                                   | 0.7              |  |  |
| Ni(2.0)                          | 960                                             | 810          | 960             | 510             | 5000                          | 88                                   | 0.8              |  |  |
| Ag(1.0)                          | 1.5                                             | 13           | 2700            | 0               | 1300                          | 99                                   | 0.7              |  |  |
| Cu(1.0)                          | 78                                              | 140          | 3000            | 0               | 2100                          | 97                                   | 0.9              |  |  |

Catalyst: 0.5 g, solution: 10 mmol L<sup>-1</sup> of an aqueous  $\text{NaNO}_3$  solution (350–370 mL), a 450 W high pressure mercury lamp, an inner irradiation quartz cell,

<sup>a</sup> Loading method of cocatalyst: impregnation and  $\text{H}_2$  reduction.

<sup>b</sup>  $(2\text{NO}_2^- + 8 \text{NH}_4^+ + 10 \text{N}_2)/(2\text{H}_2 + 2\text{NO}_2^- + 8 \text{NH}_4^+ + 10 \text{N}_2) \times 100$ .

<sup>c</sup>  $(2\text{N}_2)/(an initial amount of \text{NO}_3^-) \times 100$ .

as an electron donor [29]. It is interesting to apply this excellent  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst to the reduction of  $\text{NO}_3^-$  employing suitable cocatalysts. We preliminary reported the reduction of  $\text{NO}_3^-$  using the  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst [30].

In the present study, photocatalytic reduction of  $\text{NO}_3^-$  into  $\text{N}_2$  was investigated using the  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst loaded with Ni cocatalyst that was effective for tantalate photocatalysts such as  $\text{KTaO}_3$ . Effects of a  $\text{H}_3\text{BO}_3$  buffer on the activity and selectivity were examined. The reaction paths were also investigated.

## 2. Experimental

### 2.1. Preparation of $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ photocatalyst and a loading method of a cocatalyst

$\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst was prepared by a polymerizable complex method according to the previously reported procedure [28,29].  $\text{BaCO}_3$  (Kanto chemical; 99.0%),  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  (Kanto chemical; 97.0%),  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Wako; 99.9%), propylene glycol (Kanto chemical; 99.0%), and citric acid (Sigma Aldrich; 99.0%) were used as starting materials. An aqueous  $\text{Ni}(\text{NO}_3)_2$  solution containing the photocatalyst was evaporated to dryness and the resulting solid was calcined at 543 K in air. Reduction treatment was performed in the presence of 200 Torr of  $\text{H}_2$  gas at 773 K for 2 h to obtain metallic Ni cocatalyst-loaded  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst.

### 2.2. Characterization

The photocatalyst was identified as a single phase by powder X-ray diffraction (Rigaku; Miniflex, Cu  $\text{K}\alpha$ ). Scanning electron microscopy (SEM) images were taken using a JEOL JSM-6700F.

### 2.3. Photocatalytic reaction

Photocatalytic  $\text{NO}_3^-$  reduction was carried out in a gas-closed circulation system using an inner irradiation quartz cell containing 350–370 mL of an aqueous  $\text{NO}_3^-$  suspension of the photocatalyst (0.5 g). pH was controlled by an addition of  $\text{H}_3\text{BO}_3$  into the suspension, if needed. A 400 W high-pressure mercury lamp was used as a light source. Gaseous products of  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{N}_2$  were determined by a gas chromatograph (Shimadzu, GC-8A) with a thermal conductivity detector (MS-5A, Ar carrier).  $\text{NO}_3^-$  of a reactant, and  $\text{NO}_2^-$  and  $\text{NH}_4^+$  of products were analyzed by an ion chromatograph (TOA-DKK, ICA-2000, DS-plus, columns for cations and anions: PCI-302S and PCI-230, eluents for cations and anions: 4 mmol/L of  $\text{HNO}_3\text{aq}$ . (pH 2.4) and a mixed solution of 0.8 mmol/L of  $\text{Na}_2\text{CO}_3\text{aq}$  and 2.4 mmol/L of  $\text{NaHCO}_3\text{aq}$ . (pH 9.9)).

## 3. Results and discussion

### 3.1. Photocatalytic reduction of $\text{NO}_3^-$ over $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ photocatalyst

**Table 1** shows  $\text{NO}_3^-$  reduction over  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst with various cocatalysts. Naked  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst gave  $\text{NO}_2^-$  and  $\text{O}_2$ . This is mainly due to not photocatalytic but photochemical reaction under UV irradiation ( $\lambda < 300$  nm) [21]. A significant decrease in  $\text{NO}_2^-$  and increases in  $\text{N}_2$ ,  $\text{NH}_4^+$ , and  $\text{H}_2$  were observed when Ni cocatalyst was loaded by an impregnation method and subsequent  $\text{H}_2$  reduction. The activity depended on the loading amount of the Ni cocatalyst. The maximum  $\text{N}_2$  yield and maximum total amounts of reacted electrons and holes were obtained at 0.5 wt% of the Ni cocatalyst.  $\text{N}_2$ ,  $\text{NH}_4^+$ , and  $\text{H}_2$  were formed by photocatalytic reactions, whereas  $\text{NO}_2^-$  formed by not only photocatalytic but also photochemical reactions.

Ag cocatalyst did not give any significant effect on the photocatalytic  $\text{NO}_3^-$  reduction, although  $\text{NO}_2^-$  formation was enhanced.  $\text{N}_2$  formation was enhanced on Cu cocatalyst-loaded  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst compared with naked  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ . Although Cu cocatalyst gave a large amount of  $\text{NO}_2^-$  than Ni cocatalyst, formations of  $\text{N}_2$  and  $\text{NH}_4^+$  were suppressed as well as  $\text{H}_2$  formation. The behaviors for  $\text{NO}_2^-$  and  $\text{NH}_4^+$  formations on the Cu cocatalyst-loaded  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst were similar to those on  $\text{Cu}/\text{TiO}_2$  in a basic aqueous solution [8]. These results were due to a large overpotential of Cu toward  $\text{H}_2$  formation.

Ni cocatalyst that was loaded by an impregnation method and subsequent  $\text{H}_2$  reduction showed high performance for the  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst. The high performance of the  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst is due to its high conduction band level, anisotropic crystal structure that enhances charge separation as observed for water splitting, and the suitable combination with a Ni cocatalyst. Kominami and co-workers have reported a high performance for  $\text{N}_2$  formation on metal-loaded  $\text{TiO}_2$  by  $\text{NO}_3^-$  and  $\text{NO}_2^-$  reduction in the presence and absence of a hole scavenger [16–18]. These reactions are not accompanied with  $\text{O}_2$  evolution, because the hole scavenger and  $\text{NO}_2^-$  are oxidized instead of  $\text{H}_2\text{O}$  molecules. This is the significant difference between the  $\text{TiO}_2$  and  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  systems. Although  $\text{O}_2$  evolution is observed for  $\text{NO}_3^-$  reduction using  $\text{Pt}/\text{TiO}_2$  photocatalyst, the main reduction product is  $\text{NH}_3$  [3]. So,  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  is a unique photocatalyst for  $\text{NO}_3^-$  reduction as well as some tantalates [21].

### 3.2. Effect of pH on photocatalytic $\text{NO}_3^-$ reduction over $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$

pH of a reactant solution changed from 7 to 12 after 10 h of a photocatalytic reaction time. The change in pH was mainly

**Table 2**

Photocatalytic  $\text{NO}_3^-$  reduction using an aqueous solution containing  $\text{H}_3\text{BO}_3$  over  $\text{Ni}/\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst.

| Ni cocatalyst<br>(wt%) <sup>a</sup> | Amounts of products after 10 h/ $\mu\text{mol}$ |                  |                   |                 | Selectivity <sup>b</sup><br>(%) | $\text{N}_2$ yield <sup>c</sup><br>(%) | $e^-/\text{h}^+$ |
|-------------------------------------|-------------------------------------------------|------------------|-------------------|-----------------|---------------------------------|----------------------------------------|------------------|
|                                     | Reduction product                               |                  |                   |                 | Oxidation product               |                                        |                  |
|                                     | $\text{H}_2$                                    | $\text{N}_2$     | $\text{NO}_2^-$   | $\text{NH}_4^+$ | $\text{O}_2$                    |                                        |                  |
| None                                | 0.5 <sup>d</sup>                                | 4.4 <sup>d</sup> | 2600 <sup>d</sup> | 0 <sup>d</sup>  | 1500 <sup>d</sup>               | 99                                     | 0.3              |
| 0.1                                 | 500                                             | 860              | 520               | 12              | 3200                            | 90                                     | 49               |
| 0.3                                 | 1000                                            | 1100             | 860               | 8.4             | 4000                            | 86                                     | 62               |
| 0.5                                 | 2400                                            | 1500             | 290               | 12              | 5500                            | 76                                     | 85               |
| 0.7                                 | 1700                                            | 1400             | 300               | 13              | 5000                            | 81                                     | 80               |

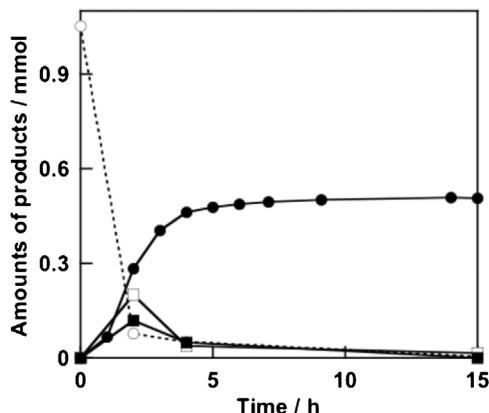
Catalyst: 0.5 g, solution: 10 mmol L<sup>-1</sup> of an aqueous  $\text{NaNO}_3$  solution containing 10 mmol L<sup>-1</sup> of  $\text{H}_3\text{BO}_3$  (350 mL, initial solution pH 6.9), a 450 W high pressure mercury lamp, an inner irradiation quartz cell,

<sup>a</sup> Loading method of cocatalyst: impregnation and  $\text{H}_2$  reduction.

<sup>b</sup>  $(2\text{NO}_2^- + 8\text{NH}_4^+ + 10\text{N}_2)/(2\text{H}_2 + 2\text{NO}_2^- + 8\text{NH}_4^+ + 10\text{N}_2) \times 100$ .

<sup>c</sup>  $(2\text{N}_2)/(an\ initial\ amount\ of\ \text{NO}_3^-) \times 100$ .

<sup>d</sup> After 6 h.



**Fig. 1.**  $\text{NO}_3^-$  reduction over  $\text{Ni}(0.5\text{ wt\%})/\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst. Catalyst: 0.5 g, solution: 3 mmol L<sup>-1</sup> of an aqueous  $\text{NaNO}_3$  solution (350 mL) containing  $\text{H}_3\text{BO}_3$  (0.6 mmol L<sup>-1</sup>),  $\text{NO}_3^-$  (○),  $\text{NO}_2^-$  (□),  $\text{NH}_4^+$  (■),  $\text{N}_2$  (●).

due to formation of  $\text{NaNO}_2$  by photochemical and photocatalytic decomposition of  $\text{NaNO}_3$ , because  $\text{NaNO}_2$  is a basic compound. Elution of a small amount of Ba may also cause the increase in pH. The pH of the reactant solution affects the activity and selectivity for photocatalytic  $\text{NO}_3^-$  reduction [1]. Therefore, a  $\text{H}_3\text{BO}_3$  buffer was used to suppress the increase in pH during photocatalytic reaction as shown in Table 2.  $\text{H}_3\text{BO}_3$  did not affect activity over naked  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ , while it enhanced  $\text{N}_2$  formation compared with the case in the absence of  $\text{H}_3\text{BO}_3$  as shown in Table 1. The effect of  $\text{H}_3\text{BO}_3$  on the photocatalytic activity was significant at a large loading amount of Ni cocatalyst.  $\text{N}_2$  formation was enhanced, while  $\text{NO}_2^-$  and  $\text{NH}_4^+$  were suppressed. This result suggested that the conversion of  $\text{NO}_2^-$  and/or  $\text{NH}_4^+$  to  $\text{N}_2$  was enhanced by suppressing an increase in pH. When 0.5% of Ni cocatalyst was loaded,  $\text{N}_2$  yield reached 85% for 10 mmol/L of an aqueous  $\text{NaNO}_3$  solution. The photocatalytic reduction of  $\text{NO}_3^-$  (3 mmol/L) on  $\text{Ni}(0.5\text{ wt\%})/\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  in the presence of  $\text{H}_3\text{BO}_3$  is shown in Fig. 1.  $\text{NO}_3^-$  was quickly consumed, and  $\text{NO}_2^-$  and  $\text{NH}_4^+$  formed at the beginning stage of the photocatalytic reaction. The  $\text{NO}_2^-$  and  $\text{NH}_4^+$  decreased with  $\text{N}_2$  formation. This result suggested that  $\text{NO}_2^-$  and  $\text{NH}_4^+$  were intermediate products for  $\text{N}_2$  formation. It should be stressed that more than 80% of  $\text{NO}_3^-$  was eliminated as  $\text{N}_2$  after 4 h of the photocatalytic reaction and almost 100% after 10 h in the present experimental condition.

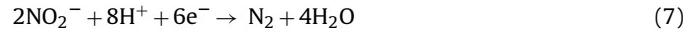
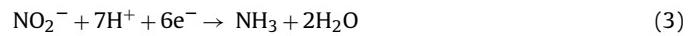
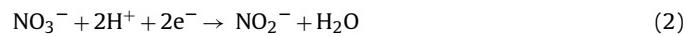
The ratio of the amount of reacted  $e^-$  to that of  $\text{h}^+$  (Eq. (1)) was almost unity, indicating that the reactions proceeded using water as an electron donor.

$$e^-/\text{h}^+ = (2\text{H}_2 + 2\text{NO}_2^- + 8\text{NH}_4^+ + 10\text{N}_2)/40\text{O}_2 \quad (1)$$

Here,  $\text{NO}_2^-$  and  $\text{O}_2$  produced by a photochemical decomposition of  $\text{NO}_3^-$  [21,30,31] were also supposed by redox reaction in Eq. (1).

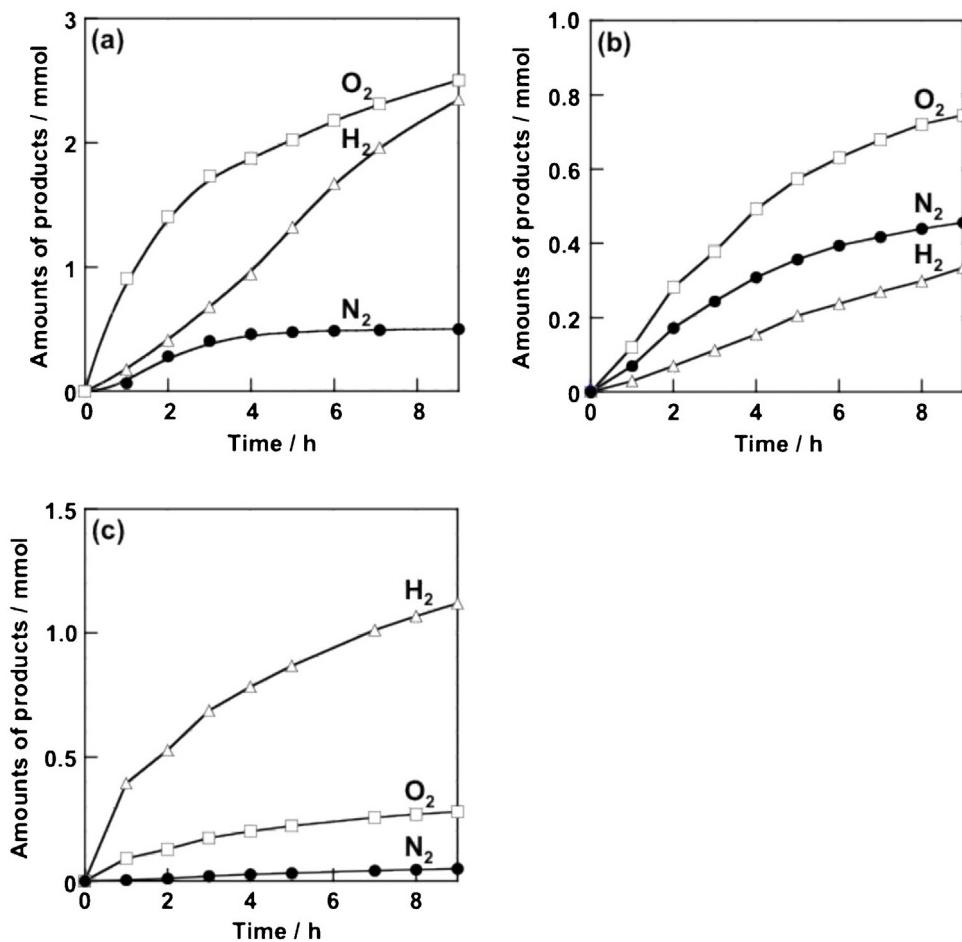
### 3.3. Plausible reaction paths of $\text{NO}_3^-$ reduction over $\text{Ni}(0.5\text{ wt\%})/\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ photocatalyst

Photocatalytic reactions on  $\text{Ni}(0.5\text{ wt\%})/\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  using aqueous solutions of  $\text{NaNO}_2$  and  $\text{NH}_4\text{Cl}$  (3 mmol/L) in addition to  $\text{NaNO}_3$  were investigated to see the reaction path of  $\text{NO}_3^-$  reduction in the presence of a  $\text{H}_3\text{BO}_3$  buffer as shown in Fig. 2. A  $\text{N}_2$  yield higher than 80% was obtained at 4 h of the photocatalytic reaction using an aqueous  $\text{NaNO}_3$  solution. Water splitting was enhanced after the consumption of  $\text{NO}_3^-$ . When the photocatalytic reaction was carried out in an aqueous  $\text{NaNO}_2$  solution, the rates of  $\text{H}_2$  and  $\text{N}_2$  formation decreased. This was mainly due to a filter effect by  $\text{NO}_2^-$  toward UV. Significant  $\text{N}_2$  evolution was not observed when an aqueous  $\text{NH}_4\text{Cl}$  solution was used, indicating that  $\text{N}_2$  formation path through oxidation of ammonium ion was negligible in the neutral aqueous solution. The reason why the ratio of  $e^-/\text{h}^+$  is deviated from the unity would be due to oxidation of slightly liberated  $\text{NH}_3$  to  $\text{NO}_3^-$  and oxidation of  $\text{Cl}^-$ . Actually,  $\text{NO}_3^-$  but not  $\text{NO}_2^-$  was detected in a liquid phase after the reaction. These results concluded the following reaction paths:

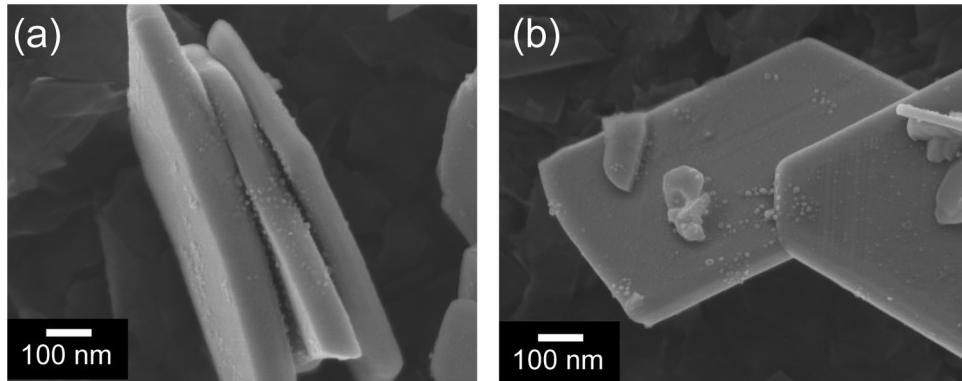


$\text{NO}_3^-$  is reduced to form  $\text{NO}_2^-$  and  $\text{NH}_3$  by photogenerated electron in the conduction band of  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  on the Ni cocatalyst as shown in Table 1 (Eqs. (2) and (3)).  $\text{NO}_2^-$  is also produced by photolysis of  $\text{NO}_3^-$  (Eq. (4)) [21,30,31]. Because pH increased to 12 in the absence of a  $\text{H}_3\text{BO}_3$  buffer after the reaction, liberated  $\text{NH}_3$  was oxidized to form  $\text{N}_2$  as observed for tantalate photocatalysts (Eq. (5)) [21]. Ammonium species mainly exists as  $\text{NH}_4^+$  in the reactant solution in the presence of the  $\text{H}_3\text{BO}_3$  buffer. The  $\text{NH}_4^+$  species reacts with  $\text{NO}_2^-$  on the Ni cocatalyst to form  $\text{N}_2$  (Eq. (6)) as reported for thermal catalysis [32].  $\text{N}_2$  could also form by further reduction of  $\text{NO}_2^-$  (Eq. (7)).  $\text{O}_2$  forms by oxidation of water (Eq. (8)) as well as photolysis of  $\text{NO}_3^-$  (Eq. (4)).

The condition of Ni cocatalyst (0.5 wt%) loaded on  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  before and after the photocatalytic reduction of  $\text{NO}_3^-$  was observed



**Fig. 2.** Gaseous products of photocatalytic reactions over  $\text{Ni}(0.5 \text{ wt\%})/\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst using  $3 \text{ mmol L}^{-1}$  of aqueous (a)  $\text{NaNO}_3$ , (b)  $\text{NaNO}_2$ , and (c)  $\text{NH}_4\text{Cl}$  solutions ( $350 \text{ mL}$ ) containing  $\text{H}_3\text{BO}_3(6 \text{ mmol L}^{-1})$ .



**Fig. 3.** SEM images of  $\text{Ni}(0.5 \text{ wt\%})/\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  (a) before and (b) after 3 h of photocatalytic reaction.

with SEM as shown in Fig. 3. As-prepared Ni cocatalyst was highly dispersed on the plate-shape surface of  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  powder. The condition of the Ni cocatalyst did not change so much after 3 h of the photocatalytic reaction time at which approximately 80% of  $\text{NO}_3^-$  was converted to  $\text{N}_2$ . This result indicated that the highly dispersed metallic Ni cocatalyst contributed to the high performance for the photocatalytic reduction of  $\text{NO}_3^-$  to  $\text{N}_2$ .

#### 4. Conclusions

Highly active  $\text{Ni}/\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst was developed for  $\text{NO}_3^-$  reduction to harmless  $\text{N}_2$  in an aqueous medium. Ni

cocatalyst-loaded  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  photocatalyst showed activity for reduction of an aqueous nitrate solution accompanied with  $\text{O}_2$  evolution without any sacrificial reagents, indicating that water was consumed as an electron donor. The conversion and selectivity of the photocatalytic reduction of  $\text{NO}_3^-$  strongly depended on the amount of Ni cocatalyst and pH of the reactant solution. The reduction of  $\text{NO}_3^-$  was enhanced compared with that of water, as the amount of Ni cocatalyst increased without pH control. The conversion of  $\text{NO}_3^-$  and the yield of  $\text{N}_2$  reached about 90 and 50% after 10 h, respectively. In this case,  $\text{N}_2$  was formed by oxidation of  $\text{NH}_3$  that was formed by reduction of  $\text{NO}_3^-$ . In the presence of a  $\text{H}_3\text{BO}_3$  buffer,  $\text{N}_2$  formed by the reaction of  $\text{NH}_4^+$  with  $\text{NO}_2^-$  on Ni co-catalyst

and also, by further reduction of  $\text{NO}_2^-$ . Thus, the photocatalytic  $\text{N}_2$  formation path in an acidic aqueous solution is different from that in a basic aqueous solution. The high photocatalytic activity for the  $\text{NO}_3^-$  reduction was caused by highly dispersed Ni cocatalyst loaded on plate shape  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  powder.

## Acknowledgement

This work was financially supported by Adaptable and Seamless Technology Transfer Program (A-STEP) through Target-driven R&D/Japan Science and Technology Agency (JST).

## References

- [1] V. Rosca, M. Duca, M.T.D. Groot, M.T.M. Koper, *Chem. Rev.* 109 (2009) 2209–2244.
- [2] M. Halmann, K. Zuckerman, *J. Chem. Soc. Chem. Commun.* (1986) 455–457.
- [3] A. Kudo, K. Domen, K. Maruya, T. Onishi, *Chem. Lett.* 16 (1987) 1019–1022.
- [4] A. Kudo, K. Domen, K. Maruya, T. Onishi, *J. Catal.* 135 (1992) 300–303.
- [5] K.T. Rangit, B. Viswanathan, *J. Photochem. Photobiol. A* 108 (1997) 73–78.
- [6] T. Sittinun, Y. Shu, T. Sato, *Int. J. Inorg. Mater.* 3 (2001) 855–859.
- [7] G. Wenliang, J. Ruicai, C. Jixin, G. Xinxin, Z. Haisheng, Z. Fuxiang, G. Naijia, *Catal. Today* 90 (2004) 331–336.
- [8] H. Kominami, T. Nakaseko, Y. Shimada, A. Furusho, H. Inoue, S. Murakami, Y. Kera, B. Ohtani, *Chem. Commun.* (2005) 2933–2935.
- [9] F. Zhang, R. Jin, J. Chen, C. Shao, W. Gao, L. Li, N. Guan, *J. Catal.* 232 (2005) 424–431.
- [10] F. Zhang, Y. Pi, J. Cui, Y. Yang, X. Zhang, N. Guan, *J. Phys. Chem. C* 111 (2007) 3756–3761.
- [11] J. Sá, C.A. Agüera, S. Gross, J.A. Anderson, *Appl. Catal. B* 85 (2009) 192–200.
- [12] L. Li, Z. Xu, F. Liu, Y. Shao, J. Wang, H. Wan, S. Zheng, *J. Photochem. Photobiol. A* 212 (2010) 113–121.
- [13] M. Yamauchi, R. Abe, T. Tsukuda, K. Kato, M. Takata, *J. Am. Chem. Soc.* 133 (2011) 1150–1152.
- [14] T. Mishra, M. Mahato, N. Aman, J.N. Patel, R.K. Sahu, *Catal. Sci. Technol.* 1 (2011) 609–615.
- [15] J.A. Anderson, *Catal. Today* 175 (2011) 316–321.
- [16] H. Kominami, A. Furusho, S. Murakami, H. Inoue, Y. Kera, B. Ohtani, *Catal. Lett.* 76 (2001) 31–34.
- [17] H. Kominami, H. Gekko, K. Hashimoto, *Phys. Chem. Chem. Phys.* 15 (2010) 423–15427, 12.
- [18] H. Gekko, K. Hashimoto, H. Kominami, *Phys. Chem. Chem. Phys.* 14 (2012) 7965–7970.
- [19] J. Cunningham, H. Zainal, *J. Phys. Chem.* 76 (1972) 2362–2374.
- [20] T. Mori, J. Suzuki, K. Fujimoto, M. Watanabe, Y. Hasegawa, *Appl. Catal. B* 23 (1999) 283–289.
- [21] H. Kato, A. Kudo, *Phys. Chem. Chem. Phys.* 4 (2002) 2833–2838.
- [22] B.A. Korgel, H.G. Monbouquette, *J. Phys. Chem. B* 101 (1997) 5010–5017.
- [23] S. Tawkaew, Y. Fujishiro, S. Yin, T. Sato, *Colloids Surf. A: Physicochem. Eng. Aspects* 179 (2001) 139–144.
- [24] J.M. Slocik, A.O. Govorov, R.R. Naik, *Angew. Chem. Int. Ed.* 47 (2008) 5335–5339.
- [25] O. Hamano, A. Kudo, *Chem. Lett.* (2002) 838–839.
- [26] I. Willner, N. Lapidot, A. Riklin, *J. Am. Chem. Soc.* 111 (1989) 1883–1884.
- [27] A. Kapoor, T. Viraraghavan, *J. Environmental Eng.* 123 (1997) 371–380.
- [28] Y. Miseki, H. Kato, A. Kudo, *Energy Environ. Sci.* 2 (2009) 2306–2314.
- [29] K. Iizuka, T. Wato, Y. Miseki, K. Saito, A. Kudo, *J. Am. Chem. Soc.* 133 (2011) 20863–20868.
- [30] M. Adachi, A. Kudo, *Chem. Lett.* 41 (2012) 1007–1008.
- [31] S. Goldstein, J. Rabani, *J. Am. Chem. Soc.* 129 (2007) 10597–10601.
- [32] Y. Yeom, M. Li, A. Savara, W. Sachtler, E. Weitz, *Catal. Today* 136 (2008) 55–63.